

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 20/02, C01B 31/08	A1	(11) International Publication Number: WO 98/31460 (43) International Publication Date: 23 July 1998 (23.07.98)
(21) International Application Number: PCT/US97/08815 (22) International Filing Date: 27 May 1997 (27.05.97) (30) Priority Data: 08/785,941 22 January 1997 (22.01.97) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint-Paul, MN 55133-3427 (US). (72) Inventor: BREY, Larry, A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: ROGERS, James, A. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: MULTI-GAS IMPREGNATED SORBENT (57) Abstract A multi-gas sorbent impregnated with a copper or zinc compound, a salt of an ammine forming metal, and a formaldehyde reactive compound. Respirator cartridges and masks employing the sorbent have improved performance.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

MULTI-GAS IMPREGNATED SORBENT

5

TECHNICAL FIELD

This invention relates to a treated sorbent. The sorbent is effective against a multiplicity of gas and vapor hazards.

10

BACKGROUND OF THE INVENTION

Air purifying gas and vapor respirators are extensively used for protection against gas and vapor hazards. These respirators contain filtering elements capable of removing toxic gases and vapors from air and means for delivering the filtered air to the breathing zone of the wearer.

15

During World War I, it was discovered that impregnating activated carbon with certain copper compounds enhanced the protection provided by activated carbon sorbents against certain war gases such as hydrogen cyanide, arsine, and phosgene. These sorbents are called whetlerites. Type A whetlerites can be prepared by depositing copper ammine carbonate in the pores of activated carbon and decomposing it to CuO by heat treatment at 150°C. Type A whetlerites are easy to prepare and are made from relatively inexpensive and readily available materials.

20

A drawback to using whetlerites is that they evolve ammonia in use, particularly when used in humid conditions. The evolution of ammonia can be uncomfortable for the user. The evolution can be minimized by drying the product at high temperature. However, drying at high temperature is expensive and care must be taken not to ignite the whetlerites.

25

In addition to the ammonia problem, Type A whetlerites typically exhibit mediocre performance against some common industrial hazards, such as formaldehyde.

30

Protection afforded by whetlerites can be extended and enhanced by incorporating additional impregnating materials, such as silver salts and hexavalent chromium as described in U.S. Patent No. 2,920,050. A review of sorbents of this

type is provided in Chapter 4 of the Summary Technical Report of Division 10, National Defense Research Committee, Office of Scientific Research and Development, Military Problems with Aerosols and Nonpersistent Gases, Washington, D. C., 1946.

5 The review also discusses the use of hexamethylenetetramine (hexamine) in a second stage impregnation. The impregnation is carried out as a separate step because the heat treatment used in the production of Type A whetlerites seriously degrades hexamine. Salts of ammine forming metals may be added with the hexamine in order to minimize ammonia evolution. However, as the concentration
10 of metal increases, so does the odor of formaldehyde, which in some cases may be more objectionable than the odor of ammonia.

 Various standards set out the gases and vapors against which filters may be tested for certification, as well as the conditions for those tests. Standards have been established and filtering elements are available for protection against specific
15 gases and vapors and against classes of gases and vapors.

 In the United States, the standards have been established by the National Institute of Occupational Safety and Health (NIOSH) against which filters may be tested for certification. These include standards for carbon tetrachloride (a
20 surrogate for the entire class of organic gases and vapors), sulfur dioxide, chlorine, hydrogen chloride, formaldehyde, hydrogen sulfide (escape only), hydrogen fluoride, chlorine dioxide, ammonia, and methylamine. In Europe, standards have been established for filters that protect against organic vapors (Type A); acid gases including hydrogen cyanide, hydrogen sulfide, and chlorine (Type B); sulfur dioxide (Type E); and ammonia (Type K).

25 Different filtering elements have been developed to meet the NIOSH and various European standards relating to multiple types of gas or vapor hazards. These elements typically contain either a mixture of sorbent materials or successive layers of two or more sorbents, each of which is effective against one or more gases or vapors. For example, U.S. Patent 5,090,407 describes a chemical cartridge for
30 protective respiratory masks having a separate active filter section and a main filter section in series with the active filter section.

Impregnation of a single sorbent against multiple hazards typically presents a problem because impregnates that work against hazards such as ammonia may damage impregnates that work against hazards such as acid gases. For example, phosphoric acid works very well against ammonia but has the unfortunate side effect of destroying impregnates that work against acid gases.

Sorbents have been made that are effective against multiple gas or vapor hazards. For example, U.S. Patent No. 4,677,096 describes an air cleaning material that the patentees claim has properties simultaneously satisfying European requirements for Types A, B, E, and K air filters. The material uses a porous substrate impregnated with zinc oxide and a water soluble salt. The water soluble salt is preferably zinc chloride, and a chromic acid salt is preferably admixed with the zinc oxide and the zinc chloride. German Patent DE 3231717 describes a sorbent capable of adsorbing both oxidizable/acidic gases and low molecular weight basic gases. The sorbent uses activated carbon impregnated with an ammine forming metal iodide, preferably zinc iodide, and also preferably containing iodine, silver nitrate, or copper sulfate. U.S. Patent No. 5,492,882 describes a material that uses activated carbon impregnated with at least one compound from each of the following three groups: (a) sulfuric acid and sulfuric acid salts, (b) molybdenum compounds, and (c) copper compounds and zinc compounds. This material is commercially available from the Calgon Carbon Corporation under the designation Calgon URC.

Despite the previous efforts to develop sorbents that are effective against multiple gas and vapor hazards, there exists a need to develop improved systems. The sorbents should not only be effective against a wide range of toxic or noxious gases and vapors, but they should do so with a minimum bulk or volume. This is because when the filter is incorporated into a respirator, greater bulk makes the respirator cumbersome and less comfortable to wear, and may interfere with vision. The filter should also exhibit a low pressure drop. Filters with a higher flow resistance are harder for the wearer to breathe through. The sorbent material should not release gases such as ammonia into the breathing zone where the wearer will inhale them. The sorbent material should also be readily manufacturable at low

cost. Preferably, the sorbent should meet relevant NIOSH or other certification standards.

SUMMARY OF THE INVENTION

5 This invention provides a sorbent useful in a respirator against a multiplicity of gases. The sorbent is a whetlerite-type sorbent having impregnated thereon at least one ammine forming metal. The sorbent is also impregnated with an amino substituted carboxylic or sulfonic salt. The sorbent may be used in a respirator cartridge as the sole sorbent or mixed or layer loaded with other sorbents, such as
10 unimpregnated carbon. In addition, the sorbent may be used in filter masks, either as the sole sorbent or mixed with other sorbents.

 This invention provides both a single stage and a two-stage impregnation method of making a multi-gas sorbent. In the single stage impregnation, the sorbent is contacted with an ammoniacal solution containing a copper and/or zinc
15 compound, ammonium carbonate or ammonium bicarbonate, the salt of an ammine forming metal, and a formaldehyde reactive compound.

 In the two-stage impregnation, the sorbent is first contacted with a solution containing a copper and/or zinc compound. In the second stage, the sorbent is contacted with a solution containing the salt of an ammine forming metal. In
20 addition, the solution in the first or second stage contains a formaldehyde reactive compound.

 This invention provides a particularly effective combination of sorbency toward a wide range of important gases and vapors to be removed from an atmosphere to be breathed. The sorbent preferably can be made to meet current
25 NIOSH standards for multi-gas sorbents with respect to sulfur dioxide, ammonia, and formaldehyde. The sorbent material can be contained in a small volume. The flow resistance through a filter made of the sorbent can be desirably low. The sorbent preferably can be made to evolve little or no ammonia odor. It has a high activity and can be mixed or layered with unimpregnated carbon to minimize cost.
30 It can be manufactured at low temperature and even at low temperature it can be made to evolve little or no ammonia odor.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The base sorbent for the present invention is carbon. The processes for deriving carbon for use in sorbents are well known in the art. The carbon may be derived from many different sources, including coconut, coal, charcoal, and coke.

5 In the present invention, activated carbon, i.e., carbon that has been treated to make it more porous and absorbent when compared to non-treated carbon, is preferred, with activated carbon derived from coconut being most preferred. The carbon may be in many forms, such as granules, pellets, fibers, or cloths. It is possible that alumina, natural and synthetic clays, silica gels, or other similar sorbents might be
10 suitable for use as a base sorbent, either alone or in combination with carbon.

The base sorbent is impregnated with either a zinc or copper compound. Copper and zinc compounds were traditionally selected for their ability to retain war gases such as phosgene and hydrogen cyanide. However, in the present invention, the zinc and copper compounds are used to impregnate the carbon for
15 reactivity against acid gases and oxidizable gases. Examples of suitable copper and zinc compounds include metallic copper, metallic zinc, copper carbonate, zinc carbonate, copper or cuprous oxide, and zinc oxide. Copper and zinc carbonate are preferred because they dissolve readily in the impregnating solution and act to stabilize it. Copper carbonate is most preferred because it is relatively inexpensive
20 and readily available.

The sorbent is also impregnated with the salt of an ammine forming metal. Suitable metals include, in addition to zinc and copper, cobalt, nickel, and iron. These compounds form complexes with ammonia, thereby eliminating it from the air that is filtered. In addition, these salts, in combination with the copper or zinc
25 compound(s), help reduce ammonia off-gassing. Suitable compounds include cobalt bromide, copper bromide, iron bromide, nickel bromide, zinc bromide, cobalt chloride, copper chloride, iron chloride, nickel chloride, zinc chloride, cobalt iodide, copper iodide, iron iodide, nickel iodide, and zinc iodide. The preferred compounds are the copper chloride and cobalt chloride compounds because of the stability of
30 the ammine complexes that are formed with these compounds. Other suitable compounds may include copper acetate, cobalt acetate, iron acetate, nickel acetate,

zinc acetate, cobalt chloroacetate, copper chloroacetate, iron chloroacetate, nickel chloroacetate, zinc chloroacetate, cobalt dichloroacetate, copper dichloroacetate, iron dichloroacetate, nickel dichloroacetate, zinc dichloroacetate, cobalt formate, copper formate, iron formate, nickel formate, zinc formate, cobalt propionate, copper propionate, iron propionate, nickel propionate, and zinc propionate.

For both the single stage and two-stage impregnations, the preferred copper or zinc compound is copper carbonate and the preferred salt of an ammine forming metal is cobalt chloride. It is believed that the combination of these two compounds may provide enhanced reactivity against sulfur dioxide in addition to the benefits realized by the present invention.

The sorbent is also impregnated with a formaldehyde reactive compound. The formaldehyde reactive compound is a primary or secondary amine bearing either zero or two carbonyl substituents attached directly to the amino nitrogen atom as disclosed in U.S. Patent No. 4,443,354 to Eian, the disclosure of which is incorporated herein by reference. The preferred formaldehyde reactive compounds are the amino substituted carboxylic salts and amino substituted sulfonic salts. Suitable amino substituted carboxylic salts include the salts of amino acids, such as potassium glycinate. Suitable amino substituted sulfonic salts include sulfanilic acid sodium salt, saccharine sodium salt, the salts of sulfamic acid (sulfamates), and metanilic acid sodium salt. The sulfamates are preferred.

The resulting sorbent exhibits reactivity against a variety of gases and vapors. The reactivity of the sorbent permits the use of lower volumes of impregnated carbon versus unimpregnated carbon in the sorbent.

The sorbent may be made in either a single or two-stage impregnation. The single stage impregnation involves soaking the base sorbent in an ammoniacal solution containing the salt of a copper and/or zinc compound, ammonium carbonate or bicarbonate, the salt of an ammine forming metal, and a formaldehyde reactive compound. The ammonium carbonate or bicarbonate is added to the solution because it helps to dissolve the copper or zinc in the solution. It is believed that other compounds exhibiting the same dissolving characteristics may be substituted for ammonium carbonate or ammonium bicarbonate, such as carbamate.

The sorbent is soaked for a period of time ranging from ten minutes to about an hour. Thereafter, the sorbent is dried at a temperature ranging between 125°C to 190°C for a period of time determined by the mass transfer of water and ammonia out of the carbon pores. It is believed that drying the sorbent at higher
5 temperatures, such as between 165°C and 190°C, helps to reduce the ammonia off-gassing.

In the two-stage technique, the base sorbent is impregnated with either a zinc or copper compound. The copper or zinc compound is dissolved in an ammoniacal impregnating solution containing sufficient ammonia to dissolve the
10 copper or zinc compound. Compounds such as ammonium carbonate may be added to assist in dissolving the zinc and copper compounds in the solution.

The sorbent is soaked in the solution ranging between ten minutes to approximately one hour. Thereafter, the excess impregnation solution may be drained off.

15 The sorbent is heated in order to dry it and, in the case of whetlerites, to convert the copper compound to copper oxide. However, in the present invention, it is not necessary to convert the copper or zinc compound to copper or zinc oxide during the heating step. Accordingly, the treated sorbent need only be heated to a temperature in the range of 110°C to 130°C. Notwithstanding the foregoing, the
20 sorbent may contain copper or zinc oxide without adversely affecting the characteristics of the sorbent. The carbon is heated until it appears dry. Additional heating may be employed to ensure that the carbon is dry and has a low level of residual ammonia.

After drying, the sorbent is contacted with the salt of an ammine forming
25 metal in a solution that is substantially free of ammonia. These compounds do not damage the initial zinc or copper impregnation because the impregnates of the first step are not significantly soluble in the substantially ammonia-free aqueous solution of the second stage impregnation. In addition, it is possible that the zinc and copper compounds react with the salts of the ammine forming metals to give activity
30 against the targeted gases and vapors.

During the salt addition, the pH may be adjusted upward, compatible with the salt compound. This adjustment helps to prevent damage to the zinc or copper impregnate of the first impregnation step because it prevents the basic impregnated salts from being extracted from the carbon.

5 The sorbent is also treated with a formaldehyde reactive compound. This compound may be added either in the first or second step.

In the resulting composition, at least one, preferably two, ammine forming metals are present in some form, such as an oxide or salt. In a preferred embodiment, both copper and cobalt are present. In addition, at least one
10 formaldehyde reactive compound is present. In the preferred embodiment, sulfamate is present.

The sorbent may be loaded into a respirator cartridge for use in respirators. Suitable cartridges and respirators include the 3M Series 5000, 3M Series 6000, and 3M Series 7000 respirators and cartridges available from available from
15 Minnesota Mining & Manufacturing Company of St. Paul, Minnesota ("3M"). The sorbent may be layer-loaded with unimpregnated sorbent. Alternatively, the sorbent of the present invention and the unimpregnated sorbent may be blended together. Additional elements may be included in the cartridge, including drying elements and filters for various hazards such as smoke.

20 The sorbent may also be incorporated into a filter mask. Representative filter masks include the 3M Series 4000 mask available from 3M. As with the cartridge, the sorbent may be mixed with an unimpregnated sorbent.

EXAMPLES

25 Copper impregnating solutions were prepared by combining deionized water, basic copper carbonate [assumed composition $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, 55.6% Cu, 2.0% CO_2], aqueous ammonia [assumed composition 29% NH_3], and ammonium carbonate [assumed composition $(\text{NH}_4)_2\text{CO}_3$, 34.2% NH_3 , 54.3% CO_2]. The solution composition is specified by specifying the percent copper, percent
30 ammonia, and percent carbon dioxide. In some cases, additional components were

added to the impregnating solutions. All component compositions are expressed as weight percentages.

5 The carbon used was Kuraray GC activated carbon from Kuraray Chemical Company, Osaka, Japan, with a US standard mesh size of 16 x 35 (0.5 mm x 1.5 mm).

Testing was performed by first loading the carbon sorbent into a commercially available 6000 Series respirator cartridge made by 3M Company. The capacity of these cartridges was 105 cubic centimeters. The loaded cartridges were then tested for service life according to various NIOSH standards for gas and vapor hazards.

10 In some cases the cartridges were filled with a layer of 50 cubic centimeters of unimpregnated activated carbon and a layer of 55 cubic centimeters of impregnated activated carbon. These samples are called layer loaded. They were tested with the impregnated layer on top, i.e., contacting the contaminated atmosphere first.

NIOSH standards specify that for a combination organic vapor/acid gas approval, the a filter must exhibit a service life as defined by the test protocol of at least 15 minutes for sulfur dioxide; at least 25 minutes for ammonia; and at least 50 minutes for formaldehyde.

20

Example 1

A copper impregnating solution was prepared as described above containing 5% copper, 5% ammonia, 7.5% carbon dioxide, and 6% sulfamic acid. To 1000 grams of this solution was added 584 grams of Kuraray GC activated carbon. After soaking for about 30 minutes, the carbon was separated from the supernatant liquid by vacuum filtration. The wet carbon was dried at 110°C with periodic stirring until it appeared dry and then was further dried at 160°C for several hours. The carbon recovered weighed 668 grams.

25 A second impregnation was carried out by soaking 335 grams of the above intermediate impregnated carbon in a 0.8 molal solution of cobalt chloride. The

30

carbon was then filtered from the supernatant liquid and dried at 140°C to a constant weight. The recovered carbon weighed 359 grams.

One hundred five cc of the impregnated carbon was loaded in a 3M Series 6000 respirator cartridge as described above and tested for sulfur dioxide service life (SO₂ S.L.), ammonia service life (NH₃ S.L.), and formaldehyde service life (Form. S.L.). Service lives are given in minutes and the results are given in Table 1. The sorbent exceeded the NIOSH standards for sulfur dioxide, ammonia, and formaldehyde.

Table 1

Example	SO ₂ S.L.	NH ₃ S.L.	Form. S.L.
1	72	128	>>180

The impregnated carbon was also layer loaded as described above by adding a layer of 55 cubic centimeters (cc) of impregnated carbon and 50 cubic centimeters of unimpregnated Kuraray GC carbon in a 3M Series 6000 respirator cartridge. The formaldehyde service life was measured in this configuration and found to be 116 minutes.

Example 2

Carbon was impregnated and dried as described in the first impregnating step in Example 1. A second impregnating step was carried out by soaking 132 grams of this intermediate impregnated carbon in a 0.8 molal solution of cupric chloride. The carbon was then filtered from the supernatant liquid and dried at 140°C for about four hours. The recovered carbon weighed 143 grams.

One hundred five cc of the impregnated carbon was loaded in a 3M Series 6000 respirator cartridge as described above and tested for service life against sulfur dioxide. The service life was 61 minutes.

The impregnated carbon was layer loaded using a layer of 55 cc of impregnated carbon and 50 cc of unimpregnated carbon as described above. The

formaldehyde service life in this configuration was measured and found to be 29 minutes.

Example 3

5 An impregnating solution was prepared as described above containing 6% copper, 9% ammonia, 6% carbon dioxide, and 5% sulfamic acid. To 18 kg of this solution was added 6 kg of Kuraray GC carbon in a laboratory treater/drier. After soaking, the excess solution was drained off and the carbon was heated over a period of 6.8 hours to 166°C. The recovered carbon weighed 6.6 kg.

10 A second impregnation was carried out by soaking 195 grams of the above intermediate impregnated carbon in 387 grams of a 0.8 molal solution of cobalt chloride which had been pH adjusted to pH 6 with potassium hydroxide. The carbon was then filtered from the supernatant liquid and dried at 110°C. The recovered carbon weighed 216 grams.

15 The impregnated carbon was layer loaded using a layer of 55 cc of impregnated carbon and 50 cc of unimpregnated carbon in a 3M Series 6000 respirator cartridge as described above and tested for service life against sulfur dioxide (SO₂ S.L.), ammonia service life (NH₃ S.L.), and formaldehyde service life (form. S.L.). Service lives are given in minutes and the results are given in Table 2.

20

Table 2

Example	SO ₂ S.L.	NH ₃ S.L.	Form. S.L.
3	28	140	85

Example 4 and Comparative Examples C1-C3

25 An impregnating solution was prepared as described above containing 6% copper, 9% ammonia, 6% carbon dioxide, and 6% sulfamic acid. To 2000 grams of this solution was added 1000 grams of Kuraray GC carbon. After soaking, the excess solution was drained off and the carbon was dried at 140°C for about four hours. The carbon recovered weighed 1149 grams.

A portion of the above intermediate impregnated carbon weighing 350 grams was redried at 165°C for several hours. A second impregnation was carried out by soaking 250 grams of the redried carbon in 500 grams of 0.8 molal solution of cobalt chloride. The carbon was then filtered from the supernatant liquid and
 5 dried at 110°C for several hours. The recovered carbon weighed 268 grams.

The impregnated carbon was loaded into a 3M Series 6000 respirator cartridge. Wet air with a relative humidity of 87% was passed through the cartridge at 16 liters per minute, and the amount of outgassed ammonia was measured over a
 5 hour period.

10 For comparison, the intermediate impregnated carbon from the first impregnation step (identified in Table 3 as sample C1) was also loaded into a similar cartridge and tested similarly. In addition, 105 cc of Calgon URC activated carbon, lot 4146 dr 24, made by Calgon Carbon Corporation, Pittsburgh, PA. ("C2"), was loaded into a similar cartridge and tested similarly. In addition, a Mine Safety
 15 Appliances Company GME cartridge, lot 1495, made by Mine Safety Appliances Company, Pittsburgh, PA. ("C3"), was tested similarly. The results are reported as parts per million ammonia in the air exiting the cartridge, and are given in Table 3.

Table 3

20 Outgassed Ammonia (in ppm) With Time (Hours)

Example	1 Hour	2 Hours	3 Hours	4 Hours	5 Hours
4	0.7	0.8	0.8	0.7	0.7
C1 (int)	1.6	1.4	1.3	1.2	1.2
C2 (Cal)	0.9	0.9	1.0	1.0	1.0
C3 (MSA)	1.3	1.3	1.3	1.3	1.2

Example 5

25 An impregnating solution was prepared as described above containing 7% copper, 10.5% ammonia, and 7% carbon dioxide. To 2000 grams of this solution was added 1000 grams of Kuraray GC carbon. After soaking, the excess solution

was drained off and the carbon was dried at 160°C to a constant weight. The recovered intermediate carbon weighed 1089 grams.

5 A second impregnation was carried out by soaking 250 grams of the above intermediate impregnated carbon in 499 grams of a solution 1.0 molal in cobalt chloride and 0.4 molal in potassium sulfamate. The carbon was then filtered from the supernatant liquid and dried at 110°C to a constant weight. The recovered carbon weighed 305 grams.

10 The impregnated carbon was layer loaded using a layer of 55 cc of impregnated carbon and 50 cc of unimpregnated carbon in a 3M Series 6000 respirator cartridge as described above and tested. Service lives are given in minutes and the results are given in Table 4.

Table 4

Example	SO ₂ S.L.	NH ₃ S.L.	Form. S.L.
5	24	50	81

15

Example 6

Carbon was impregnated as described in the first impregnating step in Example 5. A second impregnation was carried out by soaking 250 grams of the above intermediate impregnated carbon in 499 grams of a solution 1.0 molal in cobalt chloride and 0.4 molar in potassium sulfamate which had been pH adjusted to pH 6 with potassium hydroxide. The carbon was then filtered from the supernatant liquid and dried at 110°C to a constant weight. The recovered carbon weighed 304 grams.

20 The impregnated carbon was layer loaded using a layer of 55 cc of impregnated carbon and 50 cc of unimpregnated carbon in a 3M Series 6000 respirator cartridge as described above and tested. Service lives are given in minutes and the results are given in Table 5.

Table 5

Example	SO ₂ S.L.	NH ₃ S.L.	Form. S.L.
6	27	49	93

Example 7

An impregnating solution was prepared as described above containing 3.8% copper, 5.8% ammonia, 3.8% carbon dioxide, and 4.0% glycine. To 500 grams of this solution was added 250 grams of Kuraray GC carbon. After soaking, the excess solution was drained off and the carbon was dried at 110°C for about four hours. A second impregnation was carried out by soaking 212 grams of the above intermediate impregnated carbon in 400 grams of a solution 0.8 molal in cobalt chloride. Excess solution was then dried at 110°C to a constant weight.

The impregnated carbon was layer loaded using a layer of 55 cc of impregnated carbon and 50 cc of unimpregnated carbon in a 3M Series 6000 respirator cartridge as described above and tested. Service lives are given in minutes and the results are given in Table 6.

Table 6

Example	SO ₂ S.L.	NH ₃ S.L.	Form. S.L.
7	19.3	37.5	33

Example 8

Four hundred fifty grams of Kuraray CG carbon was treated with a solution prepared by dissolving 135 grams of basic copper carbonate [assumed composition $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, 55.6% Cu, 2.0% CO_2], 133 grams of ammonium carbonate [assumed composition $(\text{NH}_4)_2\text{CO}_3$, 34.2% NH_3 , 54.3% CO_2] 80 grams of cobalt chloride hexahydrate, and 38.8 grams of sulfamic acid in a solution prepared by mixing 257 grams of ammonia water [assumed composition 29% NH_3] and 298 grams of deionized water. The excess solution was drained off and the carbon dried at 140°C. 545 grams of treated carbon was recovered.

The impregnated carbon was layer loaded using a layer of 55 cc of impregnated carbon and 50 cc of unimpregnated carbon in a 3M Series 6000 respirator cartridge as described above and tested. Service lives are given in minutes and the results are given in Table 7.

5

Table 7

Example	SO ₂ S.L.	NH ₃ S.L.	Form. S.L.
8	120	45	>>150

10 This invention may take on various modifications and alterations without departing from the spirit and scope thereof. Accordingly, it is to be understood that this invention is not to be limited to the above-described, but it is to be controlled by the limitations set forth in the following claims and any equivalents thereof. It is also to be understood that this invention may be suitably practiced in the absence of any element not specifically disclosed herein.

What is claimed is:

1. A carbon sorbent impregnated with a compound selected from the group consisting of copper and zinc compounds, an ammine forming metal, and a compound selected from the group consisting of amino substituted carboxylic salts and amino substituted sulfonic salts.
2. The sorbent of claim 1 wherein the carbon is impregnated by contacting the sorbent with ammoniacal copper, cobalt chloride, and sulfamate.
3. A single stage impregnation method of preparing the multi-gas sorbent of claim 1 comprising contacting a base sorbent with a solution containing a compound selected from the group consisting of copper compounds and zinc compounds, a salt of an ammine forming metal, and a compound selected from the group consisting of amino substituted carboxylic salts and amino substituted sulfonic salts.
4. The method of claim 3 wherein the solution contains sulfamate.
5. A two-stage impregnation method for preparing the multi-gas sorbent of claim 1 comprising a first stage wherein a base sorbent is contacted with a solution containing a compound selected from the group consisting of copper and zinc compounds and a second stage wherein the base sorbent is contacted with a solution containing a salt of an ammine forming metal and either the solution of the first stage or the solution of the second stage contains a compound selected from the group consisting of amino substituted carboxylic salts and amino substituted sulfonic salts.
6. The method of claim 5 wherein the solution of the second stage contains cobalt chloride and sulfamate.

7. A filter mask containing the carbon sorbent of claim 1 impregnated with a copper or zinc compound, at least one ammine forming metal, and a compound selected from the group consisting of amino substituted carboxylic salts and amino substituted sulfonic salts.

5

8. The filter mask of claim 7 wherein the mask contains a sorbent impregnated with copper, cobalt, and sulfamate.

9. A multi-gas respirator filter cartridge containing the carbon sorbent of claim 1 impregnated with a zinc or copper compound, a salt of an ammine forming metal, and a compound selected from the group consisting of amino substituted carboxylic acids and amino substituted sulfonic salts.

10. A respirator filter cartridge containing carbon impregnated with a copper compound, a salt of an ammine forming metal, and sulfamate.

11. A multi-gas sorbent impregnated by contacting a base sorbent with a compound selected from the group consisting of copper and zinc compounds, a salt of an ammine forming metal, and a formaldehyde reactive compound.

20

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 97/08815

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01J 20/02, C01B 31/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01J, C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0629437 A1 (THE MINISTER OF NATIONAL DEFENCE OF HER MAJESTY'S CANADIAN GOVERNMENT), 21 December 1994 (21.12.94), page 1, line 4 - line 11; page 1, line 28 - line 32; page 3, line 56 - page 4, line 15 --	1-11
Y	WO 9310896 A1 (CALGON CARBON CORPORATION), 10 June 1993 (10.06.93), page 7, line 21 - line 31; page 8, line 17 - line 22, claims 1-44 --	1-11
Y	US 4443354 A (GILBERT L. EIAN), 17 April 1984 (17.04.84), column 5, line 67 - column 6, line 2, abstract --	1-11

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

- * Special categories of cited documents
- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Z document member of the same patent family

Date of the actual completion of the international search

16 Sept. 1997

Date of mailing of the international search report

10. 10. 97

Name and mailing address of the ISA/



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel.: (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

INGER LÖFGREN

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 97/08815

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0405404 A1 (CALGON CARBON CORPORATION), 2 January 1991 (02.01.91), page 3, line 12 - line 16; page 3, line 21 - line 37; page 12, line 47 - line 58 ---	1-11
A	FR 2728476 A1 (SOCIETE NOUVELLE D APPAREILS DE PROTECTION SOCIETE ANONYME), 28 June 1996 (28.06.96), abstract ---	1-11
A	DE 3231717 A1 (DRÄGERWERK AG), 1 March 1984 (01.03.84), abstract -----	1-11

INTERNATIONAL SEARCH REPORT
Information on patent family members

01/09/97

International application No.
PCT/US 97/08815

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0629437 A1	21/12/94	CA 2098513 A FI 942788 A US 5462908 A	17/12/94 17/12/94 31/10/95
WO 9310896 A1	10/06/93	CA 2124192 A EP 0614400 A JP 7501743 T US 5492882 A	10/06/93 14/09/94 23/02/95 20/02/96
US 4443354 A	17/04/84	AU 570629 B AU 1284083 A CA 1187063 A DE 3373871 A EP 0090563 A,B JP 3037973 B JP 58177139 A	24/03/88 29/09/83 14/05/85 05/11/87 05/10/83 07/06/91 17/10/83
EP 0405404 A1	02/01/91	AU 642653 B AU 5782990 A DE 69005374 D,T ES 2049866 T IL 94853 A JP 3114534 A JP 8017938 B NO 178142 B,C US 5063196 A	28/10/93 03/01/91 26/05/94 01/05/94 30/03/95 15/05/91 28/02/96 23/10/95 05/11/91
FR 2728476 A1	28/06/96	NONE	
DE 3231717 A1	01/03/84	BE 897399 A FR 2532188 A,B NL 8300805 A SE 8301988 A	14/11/83 02/03/84 16/03/84 27/02/84